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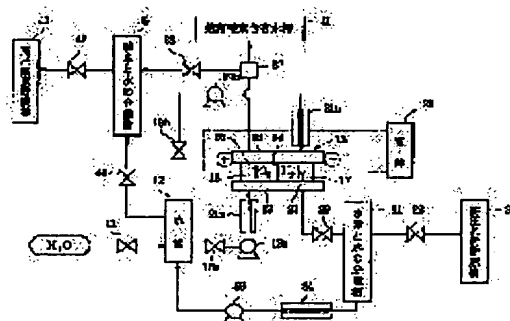
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(54) PRODUCTION OF HIGH-PRESSURE GASEOUS HYDROGEN

(57)Abstract:

PROBLEM TO BE SOLVED: To make it possible to suppress liquid resistance without adding a large amt. of electrolyte and to easily produce gaseous hydrogen of a high pressure with high electrolytic efficiency.

SOLUTION: Water is supplied to an anode chamber 16 and cathode chamber 17, respectively, which are partitioned by an insulative diaphragm 14 which is permeable to H^+ ions and OH^- ions but have poor air permeability. An electrolysis is effected by maintaining the water of the anode chamber 16 and the cathode chamber 17 in a subcritical state and supercritical state, respectively. Either or both of the pressure or temp. of the water contg. the gaseous hydrogen in the subcritical state or supercritical state generated in the anode chamber 17 is lowered, by which the gaseous hydrogen of the high pressure is taken out.



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CLAIMS

[Claim(s)]

[Claim 1] The process which supplies water to the anode plate room (16) divided with the insulating diaphragm with scarce permeability (14), and a cathode room (17), respectively although H^+ ion and OH^- ion are penetrated, The process which electrolyzes by changing the water of said anode plate room (16) and a cathode room (17) into a subcritical state or a supercritical condition, respectively, The manufacture approach of high-pressure hydrogen gas including the process which takes out high-pressure hydrogen gas by reducing either or the both sides of the pressure of the water containing the hydrogen gas of the subcritical state produced at said cathode room (17), or a supercritical condition, or temperature.

[Claim 2] The manufacture approach of the high-pressure hydrogen gas according to claim 1 added to the water supplied to an anode plate room (16) and a cathode room (17) after cooling the residual liquor which took out high-pressure hydrogen gas.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the approach of electrolyzing the water of a subcritical state or a supercritical condition, and manufacturing high-pressure hydrogen gas.

[0002]

[Description of the Prior Art] Manufacture of the hydrogen by electrolysis is performed for many years. room temperature [after adding a lot of electrolytes (for example, number - alkali, such as dozens of% of sodium hydroxide and a potassium hydroxide) in water in order to raise the conductivity of water in a conventional method since conductivity is bad when electrolyzing water] - 100 -- it energizes by the pressure of the temperature of dozens of degrees C, and ordinary pressure - 10 atmospheric pressure, and hydrogen gas is manufactured.

[0003]

[Problem(s) to be Solved by the Invention] However, by the above-mentioned conventional approach, the hydrogen gas generated by electrolysis exists as air bubbles in underwater and an electrode surface, and has the problem on which these air bubbles increase liquid resistance (electric resistance value of a liquid), and reduce electrolysis effectiveness. Moreover, since it is necessary to add a lot of electrolytes, there is un-arranging [for which a manufacturing cost increases]. Furthermore, to manufacture high-pressure hydrogen gas, it is necessary to pressurize the hydrogen gas produced in electrolysis. The purpose of this invention can control liquid resistance, without adding a lot of electrolytes, and is to offer the approach of manufacturing high-pressure hydrogen gas easily at high electrolysis effectiveness.

[0004]

[Means for Solving the Problem] The process which supplies water to the anode plate room 16 divided with the insulating diaphragm 14 with scarce permeability, and the cathode room 17, respectively although invention concerning claim 1 penetrates H⁺ ion and OH⁻ ion as shown in drawing 1 , The process which electrolyzes by changing the water of the anode plate room 16 and the cathode room 17 into a subcritical state or a supercritical condition, respectively. It is the manufacture approach of high-pressure hydrogen gas including the process which takes out high-pressure hydrogen gas by reducing either or the both sides of the pressure of the water containing the hydrogen gas of the subcritical state produced at the cathode room 17, or a supercritical condition, or temperature. Since the water of a subcritical state or a supercritical condition has a diffusing capacity superior to usual water and the mass transfer in an electrode surface happens promptly, the hydrogen gas generated in the electrode surface of the cathode room 17 forms promptly the water and the homogeneity phase which are the electrolytic solution. Consequently, the amount of air bubbles of the hydrogen gas generated in the amount of air bubbles of the hydrogen gas generated in the above-mentioned electrode surface and the electrolytic solution falls, and liquid resistance is controlled. Moreover, since a reaction rate becomes large according to an elevated temperature, electrolysis effectiveness improves. Furthermore, high-pressure hydrogen gas is obtained after electrolysis, without establishing a special-pressurization means.

[0005] Invention concerning claim 2 is invention concerning claim 1, and after it cools the

residual liquor which took out high-pressure hydrogen gas, it is the manufacture approach of the high-pressure hydrogen gas added to the water supplied to the anode plate room 16 and the cathode room 17. The residual liquor which took out high-pressure hydrogen gas is reused as some electrolytic solutions.

[0006]

[Embodiment of the Invention] In this invention, the subcritical state of water means the condition of the water which is 200–374 degrees C in temperature, and is in the pressure of 160–215kg/cm². Moreover, the supercritical condition of water means the condition of the water which is 374–400 degrees C in temperature, and is in the pressure of 215–300kg/cm². A reaction is slow and electrolysis effectiveness is not good at under the lower limit of the temperature in a subcritical state, and a pressure. Moreover, if the upper limit of the temperature in a supercritical condition and a pressure is exceeded, a load is applied to a reaction container too much, and this is not efficient, either.

[0007] When enforcing the manufacture approach of the high-pressure hydrogen gas of this invention, equipment as shown in drawing 1 is used. Water (H₂O) is first supplied to a tank 12 through a bulb 11. The water stored in this tank 12 is supplied to the reaction container 13. The reaction container 13 has the anode plate room 16 and the cathode room 17 which were divided by the insulating diaphragm 14. The water of a tank 12 is specifically pressurized by the anode plate room 16 of the reaction container 13 by pump 19a through bulb 18a, and it is heated by pre-heater 21a, and it will be in a subcritical state or a supercritical condition, and will be fed. On the other hand, the water of a tank 12 is pressurized by the cathode room 17 by pump 19b through bulb 18b, and it is heated by pre-heater 21b, and it will be in a subcritical state or a supercritical condition, and will be fed. The heater 23 which heats the water in the anode plate room 16 and the cathode room 17 is formed in the perimeter of the reaction container 13, and, as for water, this maintains a subcritical state or a supercritical condition in the reaction container 13. The cathode 27 inserted in the anode plate 26 and the cathode room 17 which were inserted in the anode plate room 16 is connected to a power source 28, respectively.

[0008] As an ingredient of the electrode which constitutes this anode plate 26 and cathode 27, a metal, solid electrolytes, etc., such as platinum, titanium, a tantalum, and an iron system, can be used. The configuration of a plate, a rod, a network, etc. is sufficient as the configuration of an electrode. Moreover, since supercritical water has the diffusing power superior to usual water, when a porous electrode is used, it has the advantage which breadth reaction effectiveness increases [the effective reaction surface area of an electrode]. Moreover, although H⁺ ion and OH⁻ ion are penetrated as an insulating diaphragm 14, permeability is scarce, for example, porosity ceramics, such as a silica and an alumina, are used. Although these insulators are porous membrane which has the aperture of a micron unit and water is passed, most of the generated hydrogen gas or oxygen gas has the property which is not passed. If it energizes to an anode plate 26 and cathode 27 in this condition, as shown in a degree type, water is electrolyzed, hydrogen gas (H₂ gas) will be generated at the cathode room 17, and oxygen gas (O₂ gas) will generate it at the anode plate room 16, respectively. Since the anode plate room 16 and the cathode room 17 are isolated by the insulating diaphragm 14, the hydrogen gas and oxygen gas which occurred are not mixed.

[0009] a cathode room -- 17: $2\text{OH}^- \rightarrow \text{H}_2\text{O} + 2\text{e}^-$ -- the water containing the hydrogen gas generated at -- + 1 / 2O_2^{**} cathode room 17 is picked out from the reaction container 13, and is sent to the separation tub 31 of hydrogen and water through a reducing valve 29. : $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2^{**}$ anode plate room 16 Here, it separates into water and high-pressure hydrogen gas by descending a pressure with a reducing valve 29. The separated high-pressure hydrogen gas is sent and saved through a bulb 32 at the high-pressure hydrogen storage tank 33. After being cooled with a condensator 34, the water separated from hydrogen gas by the separation tub 31 of hydrogen and water is pressurized with a pump 36, is collected by the tank 12, and is reused as the electrolytic solution of the reaction container 13.

[0010] It is taken out from the reaction container 13, on the other hand, a distributing valve 37 reaches, and the water which, on the other hand, contains the oxygen gas which occurred at the anode plate room 16 is sent to the separation tub 39 of oxygen and water through a reducing

valve 38. Here, it separates into water and oxygen gas by descending a pressure with a reducing valve 38. The water containing the oxygen gas which passed through another side of a distributing valve 37 is sent and saved in the saturation oxygen content tank 41. The saturation oxygen content water of this tank 41 is used for liquefaction of coal etc. The separated high-pressure oxygen gas is sent and saved through a bulb 42 at the high-pressure-oxygen storage tank 43, and the water separated from oxygen gas by the separation tub 39 is collected by the tank 12 through a bulb 44, and is reused as the electrolytic solution of the reaction container 13.

[0011]

[Effect of the Invention] Water is supplied to the anode plate room and cathode room which H^+ ion and OH^- ion were penetrated according to this invention as stated above, but were divided with the insulating diaphragm with scarce permeability, respectively. It electrolyzes by changing the water of an anode plate room and a cathode room into a subcritical state or a supercritical condition, respectively. Since high-pressure hydrogen gas was taken out by reducing either or the both sides of the pressure of the water containing the hydrogen gas of the subcritical state produced at the cathode room, or a supercritical condition, or temperature The amount of air bubbles of the hydrogen gas generated in the amount of air bubbles of the hydrogen gas generated in an electrode surface and the electrolytic solution falls, and liquid resistance is controlled. Moreover, electrolysis effectiveness can be raised, without adding a lot of electrolytes like a conventional method. Moreover, high-pressure hydrogen gas is obtained, without establishing the pressurization means by which it is special after electrolysis.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The block diagram of the manufacturing installation of the high-pressure hydrogen gas of this invention.

[Description of Notations]

14 Insulating Diaphragm

16 Anode Plate Room

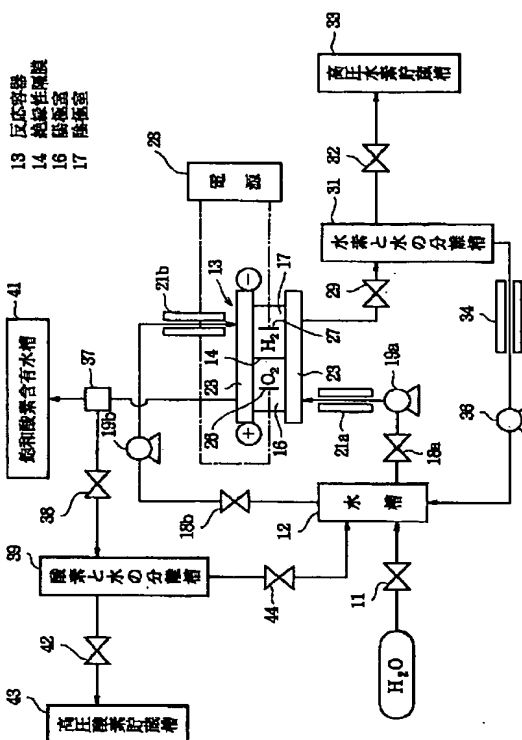
17 Cathode Room

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DOCUMENT 1/1
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Drawing selection Representative drawing



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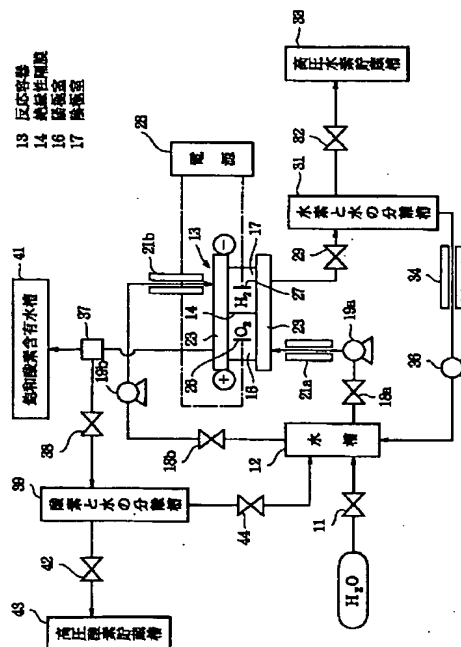
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(54) 【発明の名称】 高圧水素ガスの製造方法

(57) 【要約】

【課題】 多量の電解質を添加せずに液抵抗を抑制することができ、高い電解効率で容易に高圧の水素ガスを製造する。

【解決手段】 H^+ イオン及び OH^- イオンを透過するが通気性の乏しい絶縁性隔膜14で仕切られた陽極室16と陰極室17にそれぞれ水を供給する。陽極室16及び陰極室17の水をそれぞれ亜臨界状態又は超臨界状態にして電気分解を行う。陰極室17で生じた亜臨界状態又は超臨界状態の水素ガスとを含む水の圧力又は温度のいずれか一方又は双方を低下させることにより高圧の水素ガスを取り出す。



【特許請求の範囲】

【請求項 1】 H^+ イオン及び OH^- イオンを透過するが通気性の乏しい絶縁性隔膜 (14) で仕切られた陽極室 (16) と陰極室 (17) にそれぞれ水を供給する工程と、前記陽極室 (16) 及び陰極室 (17) の水をそれぞれ亜臨界状態又は超臨界状態にして電気分解を行う工程と、前記陰極室 (17) で生じた亜臨界状態又は超臨界状態の水素ガスを含む水の圧力又は温度のいずれか一方又は双方を低下させることにより高圧の水素ガスを取り出す工程とを含む高圧水素ガスの製造方法。

【請求項 2】 高圧の水素ガスを取り出した残液を冷却した後、陽極室 (16) 及び陰極室 (17) に供給する水に加える請求項 1 記載の高圧水素ガスの製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は亜臨界状態又は超臨界状態の水を電気分解して高圧水素ガスを製造する方法に関するものである。

【0002】

【従来の技術】 電気分解による水素の製造は古くから行われている。水を電解する場合、導電性が悪いので、従来法では水の導電性を高めるために多量の電解質（例えば数～数十％の水酸化ナトリウム、水酸化カリウム等のアルカリ）を水に添加した後、室温～百数十℃の温度、常圧～10気圧の圧力で通電して水素ガスを製造している。

【0003】

【発明が解決しようとする課題】 しかし、上記従来方法では電解によって発生する水素ガスは水中及び電極表面において気泡として存在し、この気泡が液抵抗（液体の電気抵抗値）を増大させて電解効率を低下させる問題がある。また多量の電解質を添加する必要があるため、製造コストが増大する不都合がある。更に高圧の水素ガスを製造する場合には、電解で生じた水素ガスを加圧する必要がある。本発明の目的は、多量の電解質を添加せずに液抵抗を抑制することができ、高い電解効率で容易に高圧の水素ガスを製造する方法を提供することにある。

【0004】

【課題を解決するための手段】 請求項 1 に係る発明は図 1 に示すように、 H^+ イオン及び OH^- イオンを透過するが通気性の乏しい絶縁性隔膜 14 で仕切られた陽極室 16 と陰極室 17 にそれぞれ水を供給する工程と、陽極室 16 及び陰極室 17 の水をそれぞれ亜臨界状態又は超臨界状態にして電気分解を行う工程と、陰極室 17 で生じた亜臨界状態又は超臨界状態の水素ガスを含む水の圧力又は温度のいずれか一方又は双方を低下させることにより高圧の水素ガスを取り出す工程とを含む高圧水素ガスの製造方法である。亜臨界状態又は超臨界状態の水は通常の水よりも優れた拡散能力を有し、電極表面での物質移動が速やかに起るため、陰極室 17 の電極表面で発生

した水素ガスは速やかに電解液である水と均一相を形成する。この結果、上記電極表面で発生する水素ガスの気泡量及び電解液中で発生する水素ガスの気泡量が低下し、液抵抗が抑制される。また高温によって反応速度が大きくなるため、電解効率が向上する。更に電解後、特別の加圧手段を設けることなく高圧の水素ガスが得られる。

【0005】 請求項 2 に係る発明は、請求項 1 に係る発明であって、高圧の水素ガスを取り出した残液を冷却した後、陽極室 16 及び陰極室 17 に供給する水に加える高圧水素ガスの製造方法である。高圧の水素ガスを取り出した残液は電解液の一部として再利用される。

【0006】

【発明の実施の形態】 本発明において、水の亜臨界状態とは 200～374℃の温度でかつ 160～215 kg/cm² の圧力にある水の状態を意味する。また水の超臨界状態とは 374～400℃の温度でかつ 215～300 kg/cm² の圧力にある水の状態を意味する。亜臨界状態における温度及び圧力の下限値未満では、反応が遅く、電解効率が良くない。また超臨界状態における温度及び圧力の上限値を超えると反応容器に負荷がかかり過ぎ、これも効率的でない。

【0007】 本発明の高圧水素ガスの製造方法を実施する場合には、例えば図 1 に示すような装置が用いられる。まず水 (H₂O) がバルブ 11 を介して水槽 12 に供給される。この水槽 12 に貯えられた水は反応容器 13 に供給される。反応容器 13 は絶縁性隔膜 14 により仕切られた陽極室 16 と陰極室 17 を有する。具体的には反応容器 13 の陽極室 16 には水槽 12 の水がバルブ 18a を介してポンプ 19a で加圧され、かつプレヒータ 21a で加熱されて亜臨界状態又は超臨界状態となって圧送される。一方陰極室 17 には水槽 12 の水がバルブ 18b を介してポンプ 19b で加圧され、かつプレヒータ 21b で加熱されて亜臨界状態又は超臨界状態となって圧送される。反応容器 13 の周囲には陽極室 16 及び陰極室 17 内の水を加熱するヒータ 23 が設けられ、これにより反応容器 13 内において水は亜臨界状態又は超臨界状態を維持する。陽極室 16 に挿入された陽極 26 及び陰極室 17 に挿入された陰極 27 はそれぞれ電源 28 に接続される。

【0008】 この陽極 26 及び陰極 27 を構成する電極の材料としては白金、チタン、タンタル、鉄系等の金属及び固体電解質等を用いることができる。電極の形状は板、棒、網等のような形状でもよい。また超臨界水は通常の水より優れた拡散能を有するため、多孔質の電極を用いた場合には電極の有効反応表面積が広がり反応効率が向上する利点がある。また絶縁性隔膜 14 としては H^+ イオン及び OH^- イオンを透過するが通気性の乏しい、例えばシリカ、アルミナ等の多孔質セラミックが用いられる。これらの絶縁体はミクロン単位の孔径を有する多

孔質膜であって、水は通過させるが、生成した水素ガスや酸素ガスは殆ど通過させない性質を有する。この状態において陽極26及び陰極27に通電すると、次式で示すように水は電気分解されて陰極室17では水素ガス(H_2 ガス)が、陽極室16では酸素ガス(O_2 ガス)がそれぞれ発生する。陽極室16と陰極室17は絶縁性隔膜14により隔離しているため、発生した水素ガスと酸素ガスが混ざり合うことはない。

【0009】陰極室17: $2H_2O + 2e^- \rightarrow 2OH^- + H_2 \uparrow$

陽極室16: $2OH^- \rightarrow H_2O + 2e^- + \frac{1}{2}O_2 \uparrow$

陰極室17で発生した水素ガスを含む水は反応容器13から取出され、減圧弁29を介して水素と水の分離槽31に送られる。ここでは減圧弁29で圧力を降下することにより水と高圧の水素ガスに分離される。分離された高圧の水素ガスはバルブ32を介して高圧水素貯蔵槽33に送られて保存される。水素と水の分離槽31で水素ガスから分離された水は冷却器34で冷却された後、ポンプ36で加圧されて水槽12に回収され、反応容器13の電解液として再利用される。

【0010】一方、陽極室16で発生した酸素ガスを含む水は反応容器13から取出され、分配弁37の一方及び減圧弁38を介して酸素と水の分離槽39に送られる。ここでは減圧弁38で圧力を降下することにより水と酸素ガスに分離される。分配弁37の他方を通過した酸素ガスを含む水は飽和酸素含有水槽41に送られて保*

* 存される。この水槽41の飽和酸素含有水は石炭の液化などに利用される。分離された高圧の酸素ガスはバルブ42を介して高圧酸素貯蔵槽43に送られて保存され、分離槽39で酸素ガスから分離された水はバルブ44を介して水槽12に回収され、反応容器13の電解液として再利用される。

【0011】

【発明の効果】以上述べたように、本発明によれば、 H^+ イオン及び OH^- イオンを透過するが通気性の乏しい絶縁性隔膜で仕切られた陽極室と陰極室にそれぞれ水を供給し、陽極室及び陰極室の水をそれぞれ亜臨界状態又は超臨界状態にして電気分解を行い、陰極室で生じた亜臨界状態又は超臨界状態の水素ガスとを含む水の圧力又は温度のいずれか一方又は双方を低下させることにより高圧の水素ガスを取り出すようにしたので、電極表面で発生する水素ガスの気泡量及び電解液中で発生する水素ガスの気泡量が低下し、液抵抗が抑制される。また従来法のように多量の電解質を加えることなく、電解効率を向上させることができる。また電解後に特別の加圧手段を設けることなく、高圧の水素ガスが得られる。

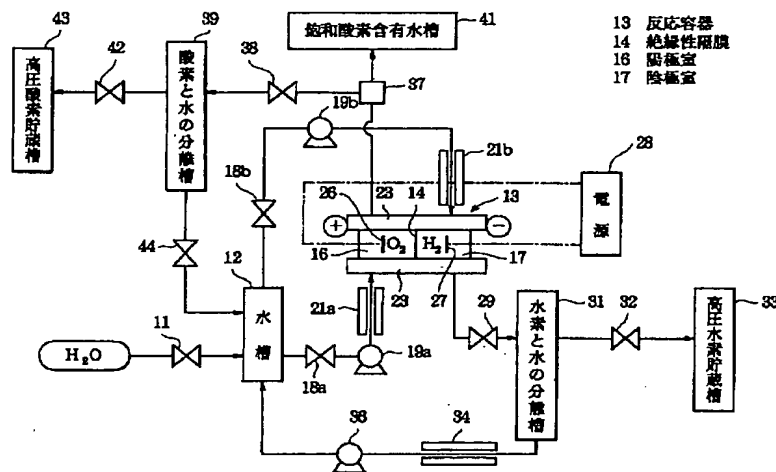
【図面の簡単な説明】

【図1】本発明の高圧水素ガスの製造装置の構成図。

【符号の説明】

14 絶縁性隔膜
16 陽極室
17 陰極室

【図1】



フロントページの続き

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